

Hot carrier and phonon dynamics in semiconductors investigated with trARPES and femtosecond electron diffraction

Shuo Dong, Samuel Beaulieu, Maciej Dendzik, Tommaso Pincelli, R. Patrick Xian, Y. William Windsor, Julian Maklar, Daniela Zahn, Helene Seiler, Thomas Vasileiadis, Yingpeng Qi, Michele Puppini, Christopher Nicholson, Lutz Waldecker, Martin Wolf, Laurenz Rettig, and Ralph Ernstorfer

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
email: ernstorfer@fhi-berlin.mpg.de, web: <https://pc.fhi-berlin.mpg.de/sesd/>

The dynamics of quasi-particles in non-equilibrium states of matter reveal the underlying microscopic coupling between electronic, spin and vibrational degrees of freedom. We aim for a quantum-state-resolved picture of coupling on the level of quasi-particle self-energies, which goes beyond established ensemble-average descriptions, and which requires ultrafast momentum-resolving techniques. The dynamics of electrons and excitons is measured with four-dimensional time- and angle-resolved photoelectron spectroscopy (trARPES), featuring a high-repetition rate XUV laser source [1] and momentum microscope detector. I will exemplify this experimental approach by discussing electron and exciton dynamics in the semiconducting transition metal dichalcogenide WSe₂ [2] and discuss its extension to nanoscale heterostructures. Our approach provides access to the transient distribution of hot carriers in the entire Brillouin zone of photo-excited semiconductors and allows the quantification of energy relaxation dynamics. The complementary view of ultrafast phonon dynamics is obtained through femtosecond electron diffraction. The elastic and inelastic scattering signal reveals the temporal evolution of vibrational excitation of the lattice and momentum-resolved information of transient phonon populations [3]. In addition, I will discuss the application of trARPES to atomic indium wires on a silicon substrate, a prototypical material system exhibiting a metal-insulator phase transition. Upon strong excitation inducing phase transitions, trARPES reveals the full transient electronic structure driving the structural transition along the reaction coordinate [4].

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Elucidating anharmonic quantum nuclear effects in hydrogen dynamics at finite temperatures

Mariana Rossi

The inclusion of anharmonic nuclear quantum effects (NQE) in electronic structure simulations has benefited from recent developments in the field of path integral molecular dynamics. We here address two of the main open challenges in this field, namely the calculation of nuclear quantum time-dependent response properties and electron-vibrational coupling, both in full-dimensionality and beyond the harmonic approximation.

We show that our developments, which can be used in all-atom/all-electron simulations, can unravel observations regarding anharmonic hydrogen transfer dynamics and isotope-effects in electronic properties. We have derived optimizations for techniques that approximate quantum dynamics and are able to describe vibrational spectra and reaction rates. These approximations are the ring-polymer instanton method [1] and thermostatted ring-polymer molecular dynamics (TRPMD) [2], which we have implemented in the i-PI code [3]. We also take advantage of an acceleration technique we have recently proposed [4], tailored for weakly-bonded organic-inorganic interfaces, to study electron-vibrational coupling through the calculation of quantum thermal averages of electronic observables.

We first address porphycene, a prototype molecular switch. We can explain the controversial coexistence of Arrhenius (classical) behaviour and strong isotope effect in its intramolecular hydrogen transfer from an interplay of a strong tunneling enhancement of the reaction that is, nevertheless, coupled to a low-frequency thermally activated mode [5]. This coupling, allied to zero-point-energy, is also responsible for an extreme broadening and red-shift of the NH-stretch band with respect to harmonic predictions, in accordance to experiments. It also causes a pronounced blue shift of this band with increasing temperature, which classical-nuclei dynamics is unable to even qualitatively describe [6]. Additionally, we explain the observed isotope-effect on the work-function changes of cyclohexane (C₆H₁₂) on Rh(111) [7], a system of relevance for catalytic dehydrogenation processes. We show how temperature and NQE cause electronic level broadening and renormalization, which is particularly pronounced for C and H/D electronic states hybridized with the surface d-band. NQE also decrease the H-Rh(111) distance, leading to a work-function change that is larger for C₆H₁₂ than C₆D₁₂.

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Near-Field Physics and Chemistry in Plasmonic STM junctions

Takashi Kumagai

Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany

Plasmonic nanogaps exhibit many intriguing properties and phenomena resulting from strong field enhancement and confinement into nanometric volumes. Recent experimental and theoretical studies have revealed the crucial role of atomistic structures and quantum mechanical effects in plasmonic nanostructures [1-3]. However, the nature of the electromagnetic field confined to the atomic scale and its interactions with matter remain poorly understood. Plasmonic STM junctions provide a unique opportunity to examine near-field-driven physics and chemistry on the atomic scale. In the talk, I will discuss our recent studies on near-field physics and chemistry in plasmonic STM junctions, including near-field-induced chemical reactions [4,5], plasmon assisted resonant electron transfer [6], engineering of localized surface plasmon resonance in STM junctions [7], and tip-enhanced resonance Raman spectroscopy [8].

References

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